

## PATENT ABSTRACTS OF JAPAN

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(21)Application number : 07-237817

(71)Applicant : TOSHIBA CHEM CORP

(22)Date of filing : 23.08.1995

(72)Inventor : WATANABE YOSHIKO  
 SHIBATA TOMOAKI

## (54) EPOXY RESIN COMPOSITION FOR CASTING

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain the an epoxy resin composition containing an epoxy resin, a specific flexibilizing agent, an inorganic filler, a specific curing agent and a cure accelerator as essential components, having excellent adhesivity, electrical characteristics, flexibility, cracking resistance and workability and useful for the insulation treatment of a high-voltage coil, etc.

SOLUTION: This epoxy resin composition contains, as essential components, (A) an epoxy resin such as a bisphenol A epoxy resin, (B) a dimer acid-modified epoxy resin as a flexibilizer, (C) a flame retardant composed of (C1) dibromocresyl glycidyl ether and (C2) antimony trioxide, (D) an inorganic filler such as silica powder, talc or hydrated alumina, (E) a curing agent composed of (E1) methyltetrahydrophthalic anhydride and (E2) a reactive polybutadiene acrylonitrile rubber and (F) a cure accelerator such as an imidazole-based agent or a t-amine-based agent.

## LEGAL STATUS

[Date of request for examination]

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 rejection]

100  
 2.9 20 flex  
 25  
 250  
 25  
 10.2 rubber  
 7% flex + rubber

AN 1997:307752 CAPLUS  
 DN 126:278385  
 ED Entered STN: 14 May 1997  
 TI Casting epoxy resin compositions having good cracking resistance, adhesion to ceramic boards, and electric properties  
 IN Watanabe, Yoshizo; Shibata, Tomoaki  
 PA Toshiba Chem Prod, Japan  
 SO Jpn. Kokai Tokkyo Koho, 4 pp.  
 CODEN: JKXXAF  
 DT Patent  
 LA Japanese  
 IC ICM C08G059-42  
 ICS B29C039-00; C08K003-22; C08K005-15; C08L063-00; H01B003-40; B29K063-00  
 CC 37-6 (Plastics Manufacture and Processing)  
 Section cross-reference(s): 76

FAN.CNT 1

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 09059349	A2	19970304	JP 1995-237817	19950823 <--
PRAI JP 1995-237817		19950823		

CLASS

PATENT NO.	CLASS	PATENT FAMILY CLASSIFICATION CODES
JP 09059349	ICM	C08G059-42
	ICS	B29C039-00; C08K003-22; C08K005-15; C08L063-00; H01B003-40; B29K063-00
	IPCI	C08G0059-42 [ICM,6]; B29C0039-00 [ICS,6]; C08K0003-22 [ICS,6]; C08K0005-15 [ICS,6]; C08L0063-00 [ICS,6]; H01B0003-40 [ICS,6]; B29K0063-00 [ICS,6]

AB The casting epoxy resin compns. contain (A) dimer acid-modified epoxy resins which give flexibility, (B) dibromocresyl diglycidyl ether (I) and Sb2O3, (C) methyltetrahydrophthalic anhydride (II) and reactive polybutadiene-acrylonitrile rubbers, and (D) cure accelerators. Application to elec. insulators of high voltage coils is indicated. Thus, a composition comprising bisphenol A glycidyl ether (25), A (50), BROCC (I) (52), H 42M (40), H 31 (70), A 1 (SiO2) (90), TSA 720 (0.1), a silane coupling agent (0.5), Sb2O3 (12), II (51.2), Hycar CTBN 1300x8 (10.2), and benzyldiethylamine (1.0) part was cured to give test pieces showing Tg 25°, volume sp. resistivity 2 + 1011 Ω-cm at 100° and DC 500 V, dielec. breakdown voltage ≥30 kV/mm, initially, and 20 kV/mm after 25 h at 121° and 2 atm, adhesion to ceramic substrates 85 kg/cm, initially, and 45 kg/cm after 50 h at 121° and 2 atmospheric

25  
 flex (50)  
 52  
 40  
 70  
 90 ST  
 0.1 IT  
 0.5  
 12  
 51.2  
 therm (10.2) IT  
 1.0  
 402  
 IT  
 15% flex + therm

casting epoxy resin ceramic substrate adhesion; dielec casting epoxy resin ceramic adhesion; elec insulator epoxy resin moisture resistance  
 Nitrile rubber, properties  
 RL: POF (Polymer in formulation); PRP (Properties); TEM (Technical or engineered material use); USES (Uses)  
 (carboxy-terminated, Hycar CTBN 1300x8; casting epoxy resin compns. having good cracking resistance, adhesion to ceramic boards, and elec. properties for elec. insulators)  
 Epoxy resins, properties  
 RL: POF (Polymer in formulation); PRP (Properties); TEM (Technical or engineered material use); USES (Uses)  
 (casting epoxy resin compns. having good cracking resistance, adhesion to ceramic boards, and elec. properties for elec. insulators)  
 Epoxy resins, properties  
 RL: POF (Polymer in formulation); PRP (Properties); TEM (Technical or engineered material use); USES (Uses)  
 (dimer acid-modified; casting epoxy resin compns. having good cracking resistance, adhesion to ceramic boards, and elec. properties for elec. insulators)  
 IT Fatty acids, properties  
 RL: POF (Polymer in formulation); PRP (Properties); TEM (Technical or

engineered material use); USES (Uses)

(dimer acids, epoxy resins; casting epoxy resin compns. having good cracking resistance, adhesion to ceramic boards, and elec. properties for elec. insulators)

IT 30171-80-3, Dibromocresyl glycidyl ether

RL: POF (Polymer in formulation); PRP (Properties); TEM (Technical or engineered material use); USES (Uses)

(BROC-C; casting epoxy resin compns. having good cracking resistance, adhesion to ceramic boards, and elec. properties for elec. insulators)

IT 772-54-3, Benzyldiethylamine 188735-72-0, Ancamine 1110

RL: CAT (Catalyst use); USES (Uses)

(casting epoxy resin compns. having good cracking resistance, adhesion to ceramic boards, and elec. properties for elec. insulators)

IT 26590-20-5, Methyltetrahydrophthalic anhydride

RL: MOA (Modifier or additive use); USES (Uses)

(casting epoxy resin compns. having good cracking resistance, adhesion to ceramic boards, and elec. properties for elec. insulators)

IT 1675-54-3

RL: PRP (Properties); TEM (Technical or engineered material use); USES (Uses)

(casting epoxy resin compns. having good cracking resistance, adhesion to ceramic boards, and elec. properties for elec. insulators)

IT 9003-18-3

RL: POF (Polymer in formulation); PRP (Properties); TEM (Technical or engineered material use); USES (Uses)

(nitrile rubber, carboxy-terminated, Hycar CTBN 1300x8; casting epoxy resin compns. having good cracking resistance, adhesion to ceramic boards, and elec. properties for elec. insulators)

DERWENT-ACC-NO: 1997-209381

DERWENT-WEEK: 199719

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TITLE: Epoxy! resin compsn for cast moulding- contains (dimer acidmodified) epoxy! resin, flame retarder, inorganic filler, curing agent, and curing promoter

PATENT-ASSIGNEE: TOSHIBA CHEM CORP[TOSM]

PRIORITY-DATA: 1995JP-0237817 (August 23, 1995)

PATENT-FAMILY:

PUB-NO	PUB-DATE	LANGUAGE	PAGES	MAINIPC
<u>JP 09059349 A</u>	March 4, 1997	N/A	004	C08G 059/42

APPLICATION-DATA:

PUB-NO	APPL-DESCRIPTOR	APPL-NO	APPL-DATE
JP 09059349A	N/A	1995JP0237817	August 23, 1995

INT-CL (IPC): B29C039/00, B29K063:00 , C08G059/42 , C08K003/22 , C08K005/15 , C08L063/00 , H01B003/40

ABSTRACTED-PUB-NO: JP 09059349A

BASIC-ABSTRACT:

Epoxy resin compsn. for cast moulding contains (A) an epoxy resin; (B) a dimer acid-modified epoxy resin as a flexibility-imparting agent; (C) a flame retarder consisting of (Ca) dibromocresyl glycidyl ether and (b) antimony trioxide; (D) inorganic filler; (E) a curing agent consisting of (Ea) methyltetrahydrophthalic anhydride and (Eb) reactive polybutadiene acrylonitrile rubber; and (F) a curing promoter as the essential components.

USE - The resin compsn. is used for insulationtreating of a high-tension coil for various kinds of electronic equipment.

ADVANTAGE - The resin compsn. has good crack resistance, adhesion and electrical characteristics.

CHOSEN-DRAWING: Dwg.0/0

TITLE-TERMS: POLYEPOXIDE RESIN COMPOSITION CAST MOULD CONTAIN DIMER ACID  
MODIFIED POLYEPOXIDE RESIN FLAME RETARD INORGANIC FILL CURE AGENT  
CURE PROMOTE

DERWENT-CLASS: A21 A85 L03 V02 X12

CPI-CODES: A04-B04; A05-A01B1; A08-D01; A08-F02; A08-F04B; A08-R01; A10-E07;  
A11-B04; A12-E01; A12-E08B; L03-A;

EPI-CODES: V02-G01C; V02-G02B1; X12-E02B;

UNLINKED-DERWENT-REGISTRY-NUMBERS: 1527U; 1694U ; 2020U

ENHANCED-POLYMER-INDEXING:

Polymer Index [1.1]

018 ; P0464\*R D01 D22 D42 F47 ; S9999 S1434

Polymer Index [1.2]

018 ; R00470 G1161 G1150 G1149 G1092 D01 D11 D10 D19 D18 D32 D50  
D76 D93 F32 F30 ; G1570\*R G1558 D01 D11 D0 D23 D22 D31 D42 D50  
D69 D73 D83 F47 7A ; H0000 ; H0011\*R ; P1898\*R P0464 D01 D10 D11

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the suitable epoxy resin constituent for notes forms excellent in crack-proof nature, the adhesive property, and the electrical property for insulating processing of the high tension coil of various electronic equipment etc.

[0002]

[Description of the Prior Art] From the former, the resin constituent for notes forms is used for insulating processing of a high-pressure transformer etc. as electronic parts of an automobile or television. And among the transformers for electronic equipment, with the epoxy resin constituent etc., the variable resistor of the flyback transformer for television etc. carries out insulating processing, and is manufactured. As for the resin constituent of these applications, crack-proof nature, flexibility, fire retardancy, the high volume resistivity at the time of an elevated temperature, and high adhesive strength are demanded. Especially in addition to these properties, recently requires severely the adhesive property with the ceramic substrate under a resistance-to-humidity condition and a thermo cycle much more. As what gives the crack-proof nature of an epoxy resin constituent, flexibility, etc., the reactant good compound is used for the DODESHINIRU succinic anhydride, the Pori azelaic-acid anhydride, and the end as a reactant curing agent.

[0003]

[Problem(s) to be Solved by the Invention] However, if this reactant curing agent is used, although flexibility will be improved, crack-proof nature is not enough and workability also has a bad fault. Moreover, in a thermo-cycle trial and a resistance-to-humidity trial, there was a fault to which an adhesive property with a ceramic substrate and an electrical property fall remarkably.

[0004] This invention was made in order to cancel the above-mentioned fault, and it tends to offer the epoxy resin constituent for notes forms excellent in crack-proof nature, flexibility, an adhesive property, fire retardancy, and electrical characteristics.

[0005]

[Means for Solving the Problem] As a result of advancing research wholeheartedly in order to attain the above-mentioned purpose, by using the below-mentioned resin constituent, this invention persons find out that the above-mentioned purpose can be attained, and complete this invention.

[0006] That is, this invention is an epoxy resin constituent for notes forms characterized by becoming (a) methyl cyclohexene-dicarboxylic anhydride of the (A) epoxy resin, the dimer acid modified epoxy resin of (B) flexibility grant agent, (a) dibromocresyl glycidyl ether of the (C) flame retarder and the (b) antimony trioxide, (D) minerals bulking agent, and the (E) curing agent, and (b) reactivity polybutadiene acrylonitrile rubber list considering the (F) hardening accelerator as an indispensable component.

[0007] Hereafter, this invention is explained to a detail.

[0008] As a (A) epoxy resin used for this invention, it is 1. To the inside of a molecule That what is necessary is just the compound which has two or more epoxy groups, there is no general-purpose epoxy resin and solid epoxy resin etc., and it can use especially a limit widely. for example, the epoxy resin

obtained by the bisphenol A mold epoxy resin, the bisphenol female mold epoxy resin, the glycidyl ether of polycarboxylic acid, and epoxidation of a cyclohexane derivative is mentioned, and these are independent -- or -- Two or more sorts can use it, mixing. Moreover, a liquefied mono-epoxy resin etc. can be used if needed other than these.

[0009] As a dimer acid modified epoxy resin of (B) flexibility grant agent used for this invention, if usually used as a flexible grant agent, there is especially no limit and it can be used widely. A dimer acid modified epoxy resin is an epoxy resin of a glycidyl ester mold, for example, Epicoat #871, #872 (oil-ized shell epoxy company make, trade name), YD-171, YD-172 (the Tohto Kasei Co., Ltd. make, trade name), etc. are mentioned. The blending ratio of coal of a flexible grant agent is the above-mentioned epoxy resin 100. It is desirable to carry out 20-50 weight section combination to the weight section. An electrical property falls remarkably and is not desirable, if the loadings of flexibility are insufficient and exceed 50 weight sections under in 20 weight sections.

[0010] As a (C) flame retarder used for this invention, (a) dibromocresyl glycidyl ether and the (b) antimony trioxide are used. If these are usually used as a flame retarder, there is especially no limit and it can be used widely. This flame retarder makes fire retardancy give a constituent, and demonstrates the synergistic effect of dibromocresyl glycidyl ether and an antimony trioxide. Dibromocresyl glycidyl ether has BROCC (Japanese powder company make, trade name) etc., and the blending ratio of coal of dibromocresyl glycidyl ether is the above-mentioned epoxy resin 100. It is desirable to carry out 15-25 weight section combination to the weight section. If the loadings exceed 25 weight sections ineffective to fire retardancy under in 15 weight sections, it is not desirable on a hardening property. Moreover, as for the blending ratio of coal of an antimony trioxide, it is desirable to carry out 7 -12 weight section combination to dibromocresyl glycidyl ether 15 - 25 weight sections. The loadings are 7. It becomes [ when 12 weight sections are exceeded ineffective to fire retardancy, there is no synergistic effect with dibromocresyl glycidyl ether, and ] cost quantity and is not desirable in under the weight section. 2 mentioned above A component may blend what mixed beforehand and was made into the flame retarder, and may carry out specified quantity combination of each component. As this flame retarder, it is important to use together (a) dibromocresyl glycidyl ether and the (b) antimony trioxide.

[0011] As a (D) minerals bulking agent used for this invention, especially if usually used as a bulking agent, it is not restricted, and it can be used widely. as a concrete thing, silica powder, talc, a hydration alumina, a calcium carbonate, etc. are mentioned, and these are independent -- or -- Two or more sorts can use it, mixing. The blending ratio of coal of a minerals bulking agent is a pitch 100. It is 100-250 to the weight section. It is desirable to carry out weight section combination. The loadings are 100. In under the weight section, crack-proof nature and heat leakage nature are bad, and since a pitch increases, it becomes cost quantity and is not desirable. Moreover, 250 It is not [ that the viscosity of a constituent is inferior to workability if the weight section is exceeded, and ] desirable.

[0012] As a (E) curing agent used for this invention, (a) methyl cyclohexene-dicarboxylic anhydride and (b) reactivity polybutadiene acrylonitrile rubber are used. It is not restricted especially that what is necessary is just what is usually used as a curing agent of an epoxy resin as methyl cyclohexene-dicarboxylic anhydride. as reactant polybutadiene acrylonitrile rubber, for example, CTBN 1300x13, 1300x8 (the Ube Industries, Ltd. make, trade name), etc. are mentioned, and these are independent -- or -- Two or more sorts can use it, mixing. The blending ratio of coal of reactant polybutadiene acrylonitrile rubber is methyl cyclohexene-dicarboxylic anhydride 100. It is desirable to carry out 15-25 weight section combination to the weight section. If the loadings have crack-proof nature and bad adhesion with an alumina substrate in under 15 weight sections and exceed 25 weight sections, the viscosity of a constituent will increase, and workability and an electrical property are bad, and it becomes cost quantity, and is not desirable.

[0013] As a (F) hardening accelerator used for this invention, things usually used as a hardening accelerator of an epoxy resin, such as an imidazole system and a tertiary amine system, can be used, and it is not restricted especially.

[0014] Although the epoxy resin constituent for notes forms used for this invention uses as an indispensable component the epoxy resin mentioned above, a flexible grant agent, a flame retarder, a

minerals bulking agent, a curing agent, and a hardening accelerator, it can carry out addition combination of the component of other minerals bulking agents, a coupling agent, a defoaming agent, a pigment, and others in the range which is not contrary to the purpose of this invention.

[0015] Each of these components, i.e., an epoxy resin, a flexible grant agent, a flame retarder, a minerals bulking agent, a curing agent, a hardening accelerator, etc. can be mixed, it can stir enough, and the epoxy resin constituent for notes forms can be manufactured. In this way, the obtained epoxy resin constituent for notes forms is used as the object for notes forms or the objects for sinking in, such as a high-pressure transformer and electronic equipment.

[0016]

[Function] The epoxy resin constituent for notes forms of this invention became possible [ holding ], without reducing an adhesive property with the ceramic substrate in the inside of a thermo cycle, and moisture-proof Shimo, and an electrical property by raising flexibility and crack-proof nature and using methyl cyclohexene-dicarboxylic anhydride and reactant polybutadiene acrylonitrile rubber as a curing agent by using a dimer acid epoxy resin as a flexible grant agent.

[0017]

[Example] Next, an example explains this invention. this invention -- these examples -- it is not limited. In the following examples and examples of a comparison, the "section" means the "weight section."

[0018] #871 (oil-ized shell epoxy company make --) of the example 1 bisphenol A glycidyl ether 25 section and a dimer acid modified epoxy resin BROCC (the Nippon Kayaku Co., Ltd. make --) of the trade name 50 section and dibromocresyl glycidyl ether The trade name 25 section, the aluminum-hydroxide H42M (Showa Denko K.K. make, trade name)40 section, A-1 (made in Tatsumori --) of the aluminum-hydroxide H31 (Showa Denko K.K. make, trade name) 70 section and a silica The trade name 90 section and defoaming agent TSA 720 (the Toshiba Silicone make, trade name) The 0.1 sections, silane coupling agent The 0.5 sections and the antimony-trioxide 12 section are mixed. subsequently -- as a curing agent -- CTBN 1300x8 (the Ube Industries, Ltd. make --) of the methyl-cyclohexene-dicarboxylic-anhydride 51.2 section and reactant polybutadiene acrylonitrile rubber It is benzyl diethylamine 1.0 as a hardening accelerator to the trade name 10.2 section and it. The section was added, it mixed enough and the epoxy resin constituent for notes forms was manufactured.

[0019] #871 (oil-ized shell epoxy company make --) of the example 2 bisphenol A glycidyl ether 40 section and a dimer acid modified epoxy resin BROCC (the Nippon Kayaku Co., Ltd. make --) of the trade name 40 section and dibromocresyl glycidyl ether The trade name 25 section, the aluminum-hydroxide H42M (Showa Denko K.K. make, trade name)30 section, A-1 (made in Tatsumori --) of the aluminum-hydroxide H31 (Showa Denko K.K. make, trade name) 80 section and a silica The trade name 90 section and defoaming agent TSA 720 (the Toshiba Silicone make, trade name) The 0.1 sections, silane coupling agent The 0.5 sections and the antimony-trioxide 12 section are mixed. subsequently -- as a curing agent -- CTBN 1300x8 (the Ube Industries, Ltd. make --) of the methyl-cyclohexene-dicarboxylic-anhydride 49.2 section and reactant polybutadiene acrylonitrile rubber The Ancamine 1110 1.0 section was added to the trade name 12.3 section and it as a hardening accelerator, it mixed enough, and the epoxy resin constituent for notes forms was manufactured.

[0020] The example bisphenol A glycidyl ether of comparison 55 section, the monoepoxide 20 section, BROCC (the Nippon Kayaku Co., Ltd. make --) of dibromocresyl glycidyl ether The trade name 25 section, the aluminum-hydroxide H42M (Showa Denko K.K. make, trade name)20 section, A-1 (made in Tatsumori --) of the aluminum-hydroxide H31 (Showa Denko K.K. make, trade name) 50 section and a silica The trade name 40 section and defoaming agent TSA 720 (the Toshiba Silicone make, trade name) The 0.1 sections, silane coupling agent The 0.5 sections and the antimony-trioxide 12 section are mixed. Subsequently, it is the dodecenyl succinic anhydride 100 as a curing agent. It is benzyl diethylamine as the section and the polybutadiene (end hydroxy group content) 40 section, and a hardening accelerator. The two sections were added, it mixed enough and the epoxy resin constituent for notes forms was manufactured.

[0021] Heat hardening was carried out using the epoxy resin constituent for notes forms manufactured by examples 1-2 and the example of a comparison. Since a glass transition point, a volume resistivity, an

adhesive property, and dielectric breakdown strength were examined about these hardened materials, the result was shown in Table 1. The effectiveness of this invention was able to be checked.

[0022]

[Table 1]

(単位)

項目	実施例		比較例
	1	2	
ガラス転移点 (°C)	25	30	45
体積抵抗率 ( $\Omega \cdot \text{cm}$ )			
[100 °C, DC500 V]	$2 \times 10^{11}$	$3 \times 10^{11}$	$3 \times 10^{13}$
絶縁破壊の強さ (kV/mm)	30以上	30以上	30以上
接着力 (kg/cm)	85	90	100
耐湿特性 [121 °C, 2atm]			
25H 放置後の絶縁破壊の強さ (kV/mm)	20	25	15
50H 後の接着力 (kg/cm)	45	50	15

[0023]

[0024]

[Effect of the Invention] Under a thermo-cycle trial and in moisture-proof Shimo, the epoxy resin constituent for notes forms of this invention has the outstanding adhesive property with a ceramic substrate, and electrical characteristics, and is excellent in flexibility and crack-proof nature, and moreover the workability of a constituent is good, and it is suitable as objects for insulating processing, such as a high tension coil of electronic equipment, so that clearly from the above explanation and Table 1.

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CLAIMS

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[Claim(s)]

[Claim 1] (A) The epoxy resin constituent for notes forms characterized by becoming (a) methyl cyclohexene-dicarboxylic anhydride of an epoxy resin, the dimer acid modified epoxy resin of (B) flexibility grant agent, (a) dibromocresyl glycidyl ether of the (C) flame retarder and the (b) antimony trioxide, (D) minerals bulking agent, and the (E) curing agent, and (b) reactivity polybutadiene acrylonitrile rubber list considering the (F) hardening accelerator as an indispensable component.

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[Translation done.]

(19)日本国特許庁 (J P)

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(11)特許出願公開番号

特開平9-59349

(43)公開日 平成9年(1997)3月4日

(51)Int.Cl. <sup>8</sup>	識別記号	庁内整理番号	F I	技術表示箇所
C 0 8 G 59/42	NHY		C 0 8 G 59/42	NHY
B 2 9 C 39/00		7726-4F	B 2 9 C 39/00	
C 0 8 K 3/22	NKV		C 0 8 K 3/22	NKV
5/15	NLA		5/15	NLA
C 0 8 L 63/00	NJN		C 0 8 L 63/00	NJN
審査請求 未請求 請求項の数1 F D (全 4 頁) 最終頁に続く				

(21)出願番号 特願平7-237817

(22)出願日 平成7年(1995)8月23日

(71)出願人 390022415

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芝ケミカル株式会社川崎工場内

(74)代理人 弁理士 諸田 英二

(54)【発明の名称】 注形用エポキシ樹脂組成物

(57)【要約】

【構成】 本発明は、(A)エポキシ樹脂、(B)可とう性付与剤のダイマー酸変性エポキシ樹脂、(C)難燃剤の(a)ジプロモクレジルグリシジルエーテルおよび(b)三酸化アンチモン、(D)無機質充填剤、(E)硬化剤の(a)メチルテトラヒドロ無水フタル酸および(b)反応性ポリブタジエンアクリロニトリルゴム並びに(F)硬化促進剤を必須成分としてなることを特徴とする注形用エポキシ樹脂組成物である。

【効果】 本発明によれば、過酷なヒートサイクル試験及び耐湿試験の条件下において、セラミック基板との優れた接着性、電気的特性を有し、可とう性、耐クラック性、作業性のよいもので高圧コイル等の絶縁処理用として好適である。

1

## 【特許請求の範囲】

【請求項1】 (A) エポキシ樹脂、

(B) 可とう性付与剤のダイマー酸変性エポキシ樹脂、

(C) 難燃剤の(a) ジブロモクレジルグリシジルエーテル及び(b) 三酸化アンチモン、

(D) 無機質充填剤、

(E) 硬化剤の(a) メチルテトラヒドロ無水フタル酸および(b) 反応性ポリブタジエンアクリロニトリルゴム並びに

(F) 硬化促進剤

を必須成分としてなることを特徴とする注形用エポキシ樹脂組成物。

## 【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は、耐クラック性、接着性、電気特性に優れた、各種電子機器の高圧コイル等の絶縁処理に好適な注形用エポキシ樹脂組成物に関する。

【0002】

【従来の技術】従来から、注形用樹脂組成物は、自動車やテレビの電子部品として高圧トランス等の絶縁処理に使用されている。そして、電子機器用トランス類のうち、テレビ用フライバックトランスの可変抵抗器等は、エポキシ樹脂組成物等で絶縁処理して製造されている。これらの用途の樹脂組成物は、耐クラック性、可とう性、難燃性、高温時の高体積抵抗率、高接着力が要求されている。特に最近では、これらの特性に加えて耐湿特性条件下及びヒートサイクル下でのセラミック基板との接着性が一段と厳しく要求されている。エポキシ樹脂組成物の耐クラック性および可とう性等を付与するものとして、ドデシル無水コハク酸やポリアゼライン酸無水物と、末端に反応性のよい化合物が反応性硬化剤として使用されている。

【0003】

【発明が解決しようとする課題】しかしながら、この反応性硬化剤を使用すると可とう性は改良されるものの、耐クラック性が十分でなく、作業性も悪い欠点がある。また、ヒートサイクル試験および耐湿特性試験において、セラミック基板との接着性、電気特性が著しく低下する欠点があった。

【0004】本発明は、上記の欠点を解消するためになされたもので、耐クラック性、可とう性、接着性、難燃性および電気的特性に優れた注形用エポキシ樹脂組成物を提供しようとするものである。

【0005】

【課題を解決するための手段】本発明者らは、上記の目的を達成しようと鋭意研究を進めた結果、後述の樹脂組成物を用いることによって、上記目的を達成できることを見いだし、本発明を完成したものである。

【0006】即ち、本発明は、

(A) エポキシ樹脂、

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(B) 可とう性付与剤のダイマー酸変性エポキシ樹脂、

(C) 難燃剤の(a) ジブロモクレジルグリシジルエーテル及び(b) 三酸化アンチモン、

(D) 無機質充填剤、

(E) 硬化剤の(a) メチルテトラヒドロ無水フタル酸および(b) 反応性ポリブタジエンアクリロニトリルゴム並びに

(F) 硬化促進剤

を必須成分としてなることを特徴とする注形用エポキシ樹脂組成物である。

【0007】以下、本発明を詳細に説明する。

【0008】本発明に用いる(A) エポキシ樹脂としては、1分子中に2個以上のエポキシ基を有する化合物であればよく、汎用エポキシ樹脂、固形エポキシ樹脂等特に制限はなく広く使用することができる。例えば、ビスフェノールA型エポキシ樹脂、ビスフェノールF型エポキシ樹脂、ポリカルボン酸のグリシジルエーテル、シクロヘキサン誘導体のエポキシ化によって得られるエポキシ樹脂等が挙げられ、これらは単独または2種以上混合して使用することができる。また、これらの他に必要に応じて液状のモノエポキシ樹脂等を使用することができる。

【0009】本発明に用いる(B) 可とう性付与剤のダイマー酸変性エポキシ樹脂としては、通常可とう性付与剤として使用されるものであれば特に制限はなく、広く使用することができる。ダイマー酸変性エポキシ樹脂は、グリシジルエステル型のエポキシ樹脂であって、例えばエピコート#871、#872(油化シェルエポキシ社製、商品名)、YD-171、YD-172(東都化成社製、商品名)などが挙げられる。可とう性付与剤の配合割合は、上述のエポキシ樹脂100重量部に対して20~50重量部配合することが望ましい。その配合量が20重量部未満では可とう性が不十分であり、また、50重量部を超えると電気特性が著しく低下して好ましくない。

【0010】本発明に用いる(C) 難燃剤としては、

(a) ジブロモクレジルグリシジルエーテルおよび

(b) 三酸化アンチモンを使用する。これらは通常難燃

剤として使用されるものであれば特に制限はなく、広く使用することができる。この難燃剤は組成物に難燃性を付与させるもので、ジブロモクレジルグリシジルエーテルと三酸化アンチモンとの相乗効果を発揮させるものである。ジブロモクレジルグリシジルエーテルは、例えばBROC-C(日本火薬社製、商品名)などがあり、ジブロモクレジルグリシジルエーテルの配合割合は、上述のエポキシ樹脂100重量部に対して、15~25重量部配合することが望ましい。その配合量が15重量部未満では難燃性に効果なく、また、25重量部を超えると硬化特性上好ましくない。また、三酸化アンチモンの配合割合は、ジブロモクレジルグリシジルエーテル15~25重量部に対して、7~12重量部配合することが望ましい。その配合

量が7重量部未満では難燃性に効果なく、また、12重量部を超えるとジプロモクレジルグリシジルエーテルとの相乗効果がなく、かつコスト高となり好ましくない。上述した2成分は予め混合して難燃剤としたものを配合してもよく、また、各成分を所定量配合してもよい。この難燃剤としては、(a)ジプロモクレジルグリシジルエーテルと(b)三酸化アンチモンを併用することが重要である。

【0011】本発明に用いる(D)無機質充填剤としては、通常充填剤として使用されるものであれば特に制限されるものでなく、広く使用することができる。具体的なものとして、シリカ粉末、タルク、水和アルミナ、炭酸カルシウム等が挙げられ、これらは単独または2種以上混合して使用することができる。無機質充填剤の配合割合は、樹脂分100重量部に対して、100～250重量部配合することが望ましい。その配合量が100重量部未満では耐クラック性、熱放散性が悪く、樹脂分が多くなるためコスト高となり好ましくない。また、250重量部を超えると組成物の粘度が増加し、作業性に劣り好ましくない。

【0012】本発明に用いる(E)硬化剤としては、(a)メチルテトラヒドロ無水フタル酸及び(b)反応性ポリブタジエンアクリロニトリルゴムを使用する。メチルテトラヒドロ無水フタル酸としては、通常エポキシ樹脂の硬化剤として使用されるものであればよく、特に制限されるものではない。反応性ポリブタジエンアクリロニトリルゴムとしては、例えば、CTBN1300×13、1300×8(宇部興産社製、商品名)等が挙げられ、これらは単独または2種以上混合して使用することができる。反応性ポリブタジエンアクリロニトリルゴムの配合割合は、メチルテトラヒドロ無水フタル酸100重量部に対して15～25重量部配合することが望ましい。その配合量が15重量部未満では耐クラック性、アルミナ基板との密着性が悪く、また、25重量部を超えると組成物の粘度が増加し、作業性、電気特性が悪く、コスト高となり、好ましくない。

【0013】本発明に用いる(F)硬化促進剤としては、イミダゾール系や3級アミン系等通常エポキシ樹脂の硬化促進剤として使用されるものを併用することができ、特に制限されるものではない。

【0014】本発明に用いる注形用エポキシ樹脂組成物は、上述したエポキシ樹脂、可とう性付与剤、難燃剤、無機質充填剤、硬化剤および硬化促進剤を必須の成分とするが、本発明の目的に反しない範囲においてその他の無機質充填剤、カップリング剤、消泡剤、顔料その他の成分を添加配合することができる。

【0015】これらの各成分すなわち、エポキシ樹脂、可とう性付与剤、難燃剤、無機質充填剤、硬化剤および硬化促進剤等を混合し、十分攪拌して注形用エポキシ樹脂組成物を製造することができる。こうして得られた注

形用エポキシ樹脂組成物は高圧トランスや電子機器等の注形用または含浸用として使用される。

【0016】

【作用】本発明の注形用エポキシ樹脂組成物は、可とう性付与剤としてダイマー酸エポキシ樹脂を用いることによって、可とう性、耐クラック性を向上させ、また、硬化剤としてメチルテトラヒドロ無水フタル酸および反応性ポリブタジエンアクリロニトリルゴムを使用することによって、ヒートサイクル中及び耐湿下におけるセラミック基板との接着性、電気特性を低下させることなく、保持することが可能となった。

【0017】

【実施例】次に本発明を実施例によって説明する。本発明はこれらの実施例によって限定されるものではない。以下の実施例および比較例において「部」とは「重量部」を意味する。

【0018】実施例1

ビスフェノールAグリシジルエーテル25部、ダイマー酸変性エポキシ樹脂の#871(油化シェルエポキシ社製、商品名)50部、ジプロモクレジルグリシジルエーテルのBROC-C(日本化薬社製、商品名)25部、水酸化アルミニウムH42M(昭和電工社製、商品名)40部、水酸化アルミニウムH31(昭和電工社製、商品名)70部、シリカのA-1(龍森社製、商品名)90部、消泡剤TSA720(東芝シリコン社製、商品名)0.1部、シランカップリング剤0.5部、および三酸化アンチモン12部を混合して、次いで硬化剤としてメチルテトラヒドロ無水フタル酸51.2部、および反応性ポリブタジエンアクリロニトリルゴムのCTBN1300×8(宇部興産社製、商品名)10.2部、それに硬化促進剤としてベンジルジエチルアミン1.0部を加えて十分混合して注形用エポキシ樹脂組成物を製造した。

【0019】実施例2

ビスフェノールAグリシジルエーテル40部、ダイマー酸変性エポキシ樹脂の#871(油化シェルエポキシ社製、商品名)40部、ジプロモクレジルグリシジルエーテルのBROC-C(日本化薬社製、商品名)25部、水酸化アルミニウムH42M(昭和電工社製、商品名)30部、水酸化アルミニウムH31(昭和電工社製、商品名)80部、シリカのA-1(龍森社製、商品名)90部、消泡剤TSA720(東芝シリコン社製、商品名)0.1部、シランカップリング剤0.5部、三酸化アンチモン12部を混合して、次いで硬化剤としてメチルテトラヒドロ無水フタル酸49.2部および反応性ポリブタジエンアクリロニトリルゴムのCTBN1300×8(宇部興産社製、商品名)12.3部、それに硬化促進剤としてアンカミン1110 1.0部を加えて十分混合して注形用エポキシ樹脂組成物を製造した。

【0020】比較例

ビスフェノールAグリシジルエーテル55部、モノエポキ

サイド20部、ジブロモクレジルグリシジルエーテルのBROC-C(日本化薬社製、商品名)25部、水酸化アルミニウムH42M(昭和電工社製、商品名)20部、水酸化アルミニウムH31(昭和電工社製、商品名)50部、シリカのA-1(龍森社製、商品名)40部、消泡剤TSA720(東芝シリコン社製、商品名)0.1部、シランカップリング剤0.5部、三酸化アンチモン12部を混合して、次いで硬化剤としてドデセニル無水コハク酸100部及びポリブタジエン(末端ヒドロキシ基含有)40部、\*

\*硬化促進剤としてベンジルジエチルアミン2部を加えて十分混合して注形用エポキシ樹脂組成物を製造した。

【0021】実施例1~2及び比較例によって製造した注形用エポキシ樹脂組成物を用いて加熱硬化させた。これらの硬化物について、ガラス転移点、体積抵抗率、接着性、絶縁破壊の強さを試験したので、その結果を表1に示した。本発明の効果を確認することができた。

【0022】

【表1】

(単位)

項目	例		比較例
	1	2	
ガラス転移点(℃)	25	30	45
体積抵抗率( $\Omega \cdot \text{cm}$ ) [100℃, DC500V]	$2 \times 10^{11}$	$3 \times 10^{11}$	$3 \times 10^{12}$
絶縁破壊の強さ(kV/mm)	30以上	30以上	30以上
接着力(kg/cm)	85	90	100
耐湿特性[121℃, 2atm]			
25H 放置後の絶縁破壊の強さ(kV/mm)	20	25	15
50H 後の接着力(kg/cm)	45	50	15

【0023】

【0024】

【発明の効果】以上の説明および表1から明らかなように、本発明の注形用エポキシ樹脂組成物は、ヒートサイ※

※クル試験中及び耐湿下において、セラミック基板との優れた接着性、電気的特性を有し、可とう性、耐クラック性に優れ、しかも作業性のよいもので電子機器の高圧コイル等の絶縁処理用として好適なものである。

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